CHEMISTRY LETTERS, pp. 1177-1178, 1977. Published by the Chemical Society of Japan

SYNTHESIS OF HEPTAMETHYLTROPYLIUM PERCHLORATE FROM 1,2,3,4,5,6,7-HEPTAMETHYLTROPILIDENE

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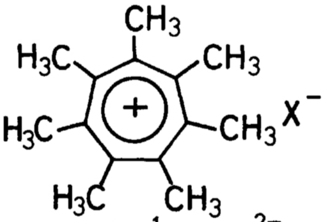
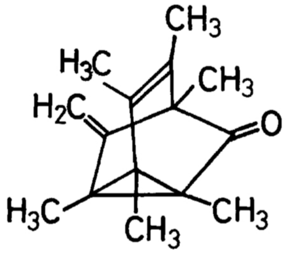
Heptamethyltropylium perchlorate has been synthesized via the reaction of 1,2,3,4,5,6,7-heptamethyltropilidene with phosphorus pentachloride and subsequent treatment with perchloric acid. The advantage of phosphorus pentachloride over triphenylcarbenium ion as a hydride-abstraction reagent is discussed.

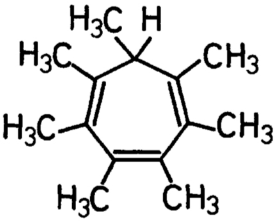
The heptamethyltropylium ion is of interest from the viewpoints of its symmetric structure of D_{7h} and the cumulative effects of the methyl substituents on the physical properties and on the reactivities. However, the isolation of pure heptamethyltropylium salts (I) has never been achieved. Peter-Katalinić, Zsindely, and Schmid found that the proton-catalyzed rearrangement of 6-methylene-1,2,3,4,5,7-hexamethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one (II) in fluorosulfonic or trifluoroacetic acid affords the heptamethyltropylium ion in low yields (4 - 14%); however, the purity of Ia thus prepared was not increased more than 60% even after many recrystallizations.1) Knoche attempted the hydride abstraction of 1,2,3,4,5,6,7-heptamethyltropilidene (III) using triphenylmethyl perchlorate or hexachloroantimonate, but no heptamethyltropylium salts were isolated, although triphenylmethane was obtained as the result of the hydride abstraction.2)



Ia: $X^- = \frac{1}{2}PtCl_6^{2-}$
Ib: $X^- = ClO_4^-$



II



III

In the course of our study of the chromium(II)-reduction of substituted tropylium ions,3) we required pure Ib. To this end, III was subjected to various methods which have been known useful for the synthesis of the unsubstituted tropylium ion from tropilidene.4-8) Among those tested, the method involving hydride transfer from III to phosphorus pentachloride7) was the only successful one for the formation of the heptamethyltropylium ion. The usual treatment of the complex salt, which is formed from III and phosphorus pentachloride with perchloric acid in ethanol or acetic acid,7) affords essentially pure crystalline Ib. A typical procedure follows.

The treatment of 0.678 g (3.56 mmol) of III[2] with 1.480 g (7.12 mmol) of phosphorus pentachloride in 10 ml of carbon tetrachloride under nitrogen for 1.5 hr at 0°C afforded yellowish white precipitates.[9] The precipitates were collected on a glass filter under a nitrogen atmosphere and then immediately dissolved in 5 ml of acetic acid containing added 0.27 ml of acetic anhydride to give a dark red solution. Addition of 0.65 ml (6.02 mmol) of 60% perchloric acid followed by precipitation with 100 ml of anhydrous ether afforded Ib as fine colorless crystals in 22% yield: mp 180 181°C;[10] NMR (CF_3COOH, 60MHz) τ = 7.23 ppm (s, CH_3's); IR (KBr) 1380, 1320, and 1090 cm^{-1}; UV_{max}(10% HCl) 260 nm (ε 49100) and 345 nm (ε 6240). Found: C, 57.83; H, 7.55% Calcd for $C_{14}H_{21}ClO_4$: C, 58.23; H, 7.33%. The perchlorate is non-hygroscopic and indefinitely stable under refrigeration. From the filtrate in the phosphorus pentachloride reaction was obtained 0.483 g of a dark brown oil including unreacted III as a main component as estimated by NMR and TLC.

The precipitates, which are formed from III and phosphorus pentachloride, are unstable, and slowly decompose consecutively as formed with evolution of hydrogen chloride; therefore it is advisable to separate the precipitates at an early stage of the reaction and to proceed to the subsequent treatment with perchloric acid. Thus, when the reaction was conducted for 3 hr at 0°C, the yield of Ib decreased to 13%; furthermore, when the reaction temperature was kept at 30°C, the precipitates, once formed, completely disappeared in 3 hr.

The reason for the success of the use of phosphorus pentachloride and the failure reported in the case of triphenylmethyl salts[2] in the hydride abstraction of III is not necessarily clear at present. The actual hydride-abstraction agent in phosphorus pentachloride has been supposed to be PCl_4^+. Presumably the sterically encumbered C_7 hydrogen of III interacts with PCl_4^+ (possibly with the positively charged chlorine) more favorably than with the carbonium carbon of triphenylcarbenium ion for steric reasons. Alternatively, the reaction might be initiated by the one-electron transfer from III to phosphorus pentachloride or PCl_4^+. In any case, the present result suggests that phosphorus pentachloride is superior to triphenylcarbenium ion as a hydride-abstraction reagent when a sterically encumbered C_7 hydrogen is to be abstracted.

References and notes

1) J. Peter-Katalinić, J. Zsindely, and H. Schmid, Helv. Chim. Acta, 56, 2796 (1973).
2) H. Knoche, Chem. Ber., 99, 1097 (1966).
3) For the latest publication, see K. Takeuchi, K. Komatsu, K. Yasuda, and K. Okamoto, Tetrahedron Lett., 1976, 3467.
4) A. P. ter Borg, R. van Helden, and A. F. Bickel, Recl. Trav. Chim. Pays-Bas, 81, 164 (1962).
5) J. V. Crivello, Synth. Commun., 3, 9 (1973), cited in Synthesis, 1973, 624.
6) D. H. Reid, M. Fraser, B. B. Molley, H. A. S. Payne, and R. G. Sutherland, Tetrahedron Lett., 1961, 530.
7) K. Conrow, Org. Synth., Coll. Vol. 5, 1138 (1973).
8) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, J. Org. Chem., 25, 1442 (1960).
9) The precipitate is presumably a double salt with a formula $(CH_3)_7C_7^+PCl_6^-\cdot(CH_3)_7C_7^+Cl^-$ from the analogy to the case of tropilidene: D. Bryce-Smith and N. A. Perkins, J. Chem. Soc., 1962, 1339.
10) The melting point is uncorrected.

(Received August 16, 1977)